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<b>(21) International Application Number:</b> PCT/US97/10419 <b>(22) International Filing Date:</b> 17 June 1997 (17.06.97)  <b>(30) Priority Data:</b> 60/020,095 17 June 1996 (17.06.96) US 60/020,199 21 June 1996 (21.06.96) US  <b>(71) Applicant:</b> EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US).  <b>(72) Inventors:</b> MATSUNAGA, Phillip, T.; 501 Davis Road No. G303, League City, TX 77573 (US). CANICH, Jo, Ann. Marie; 900 Henderson Avenue #808, Webster, TX 77058 (US). VAUGHAN, George, Alan; 3606 Durhill Street, Houston, TX 77025 (US). GINDELBERGER, David, Edward; 2 Morgan Court, Bedminster, NJ 07921 (US). SCHIFFINO, Rinaldo, S.; 4215 Meadow Forest Lane, Kingwood, TX 77345 (US). SQUIRE, Kevin, Richard; 2111 Seven Maples Drive, Kingwood, TX 77345 (US). TEMME, Rolf, Bodo; Ahornweg 7, D-41540 Dormagen (DE).  <b>(74) Agents:</b> MULLER, William, G.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US) et al.		<b>(81) Designated States:</b> AU, CA, CN, HU, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> ELEVATED PRESSURE POLYMERIZATION PROCESSES WITH LATE TRANSITION METAL CATALYST SYSTEMS		
<b>(57) Abstract</b>  The invention encompasses late transition metal catalyst systems and their use in polymerization processes, particularly in solution, 2-phase suspension and super-critical phase polymerization of ethylene-containing polymers. Preferred embodiments include the use of a late transition metal catalyst system comprising a Group 9, 10, or 11 metal complex stabilized by a bidentate ligand structure for polymerization under elevated ethylene pressure, or concentration, conditions.		

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## ELEVATED PRESSURE POLYMERIZATION PROCESSES WITH LATE TRANSITION METAL CATALYST SYSTEMS

5           This application is based on U.S. provisional applications 60/020,095, filed 06/17/96,  
and 60/020,199, filed 06/21/96.

### Field of the Invention

10           This invention relates to polymerization of olefins using late transition metal  
catalyst systems.

### Background of the Invention

15           Early transition metal catalysts for olefin polymers by coordination polymerization  
are well-known, typically those are the traditional Ziegler-type catalysts based on Group 4  
and 5 of the Periodic Table (IUPAC new nomenclature) and the newer metallocene  
catalysts based on Group 4 - 6 metals. However, specific late transition metal catalysts  
suitable for olefin polymerization had not offered the same levels of activity or molecular  
weight capability for olefin polymerization during the development of these catalyst  
systems and additional work was published addressing this lack.

20

          In Johnson, Killian, and Brookhart, *J. Am. Chem. Soc.*, 1995, 117, 6414 the  
reporters describe the use of Ni and Pd complexes for the solution homopolymerization of  
ethylene, propylene, and 1-hexene. The catalyst precursors are square-planar,  $M^{2+}$ ,  $d^8$ ,  
16 electron complexes incorporating substituted, bidentate diimine ligands. The active  
25 coordination sites are occupied by either methyl or bromide ligands. Methyl ligand  
complexes were activated with  $H^+(OEt)_2[B(3,5-(CF_3)_2C_6H_3)_4]^-$  and bromide ligand  
complexes were activated with methylalumoxane (MAO) or diethylaluminumchloride as  
cocatalysts. All examples are solution process examples, the illustrated process  
temperatures do not exceed 25 °C. Examples 6 and 7 illustrate a significant increase in  
30 branching and significant decreases in  $M_n$  and  $T_m$  (by differential scanning calorimetry)  
when the illustrated solution process temperature is raised from 0 °C to 25 °C.

Homogeneous processes such as high temperature solution and high pressure, high temperature polymerization processes, such as those at 500 bar and above, have shown particular suitability with metallocene systems. These processes allow for the improved productivity that occurs with greater reactivities at high temperature, the high pressure maintaining an essentially single phase reaction medium while permitting the higher temperatures. See, U.S. patent 5,408,017 and its equivalent WO-A-93/05732, and EP-A1-0 612 768. In this last document, bridged and unbridged hafnium metallocene compounds stabilized by non-coordinating anions after activation with alkyl-aluminum are utilized in processes at temperatures exceeding 120 °C. These solution processes are preferably to be conducted at pressures of 500 to 3500 kg/cm<sup>2</sup>.

In view of the process advantages associated with high temperature processes, it is industrially desirable to identify conditions under which late transition metal olefin polymerization catalysts can be effectively utilized.

### **Summary of Invention**

The invention comprises a process for the polymerization of ethylene polymers comprising contacting ethylene and optionally, one or more of C<sub>3</sub>-C<sub>20</sub>  $\alpha$ -olefins, C<sub>4</sub>-C<sub>20</sub> diolefins, ethylenically unsaturated polar monomers, and other suitable monomers, with an unsupported late transition metal catalyst system at elevated ethylene pressures, preferably at least 60 psia (413.7 kPa). Typically the contacting can be practiced in a solvent or suspension process in a solvent or diluent wherein the temperature is at least 30°C. Additionally the process of the invention can be practiced with or without diluent or solvent in an elevated pressure process wherein said contacting is done at a temperature of at least 120°C and a pressure of at least 50 bar (5000 kPa).

### Detailed Description of the Invention

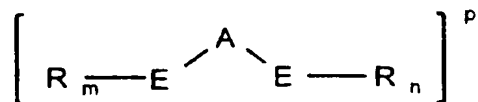
The polymerization catalysts of this invention can be derived from the late transition metal compounds of formula:

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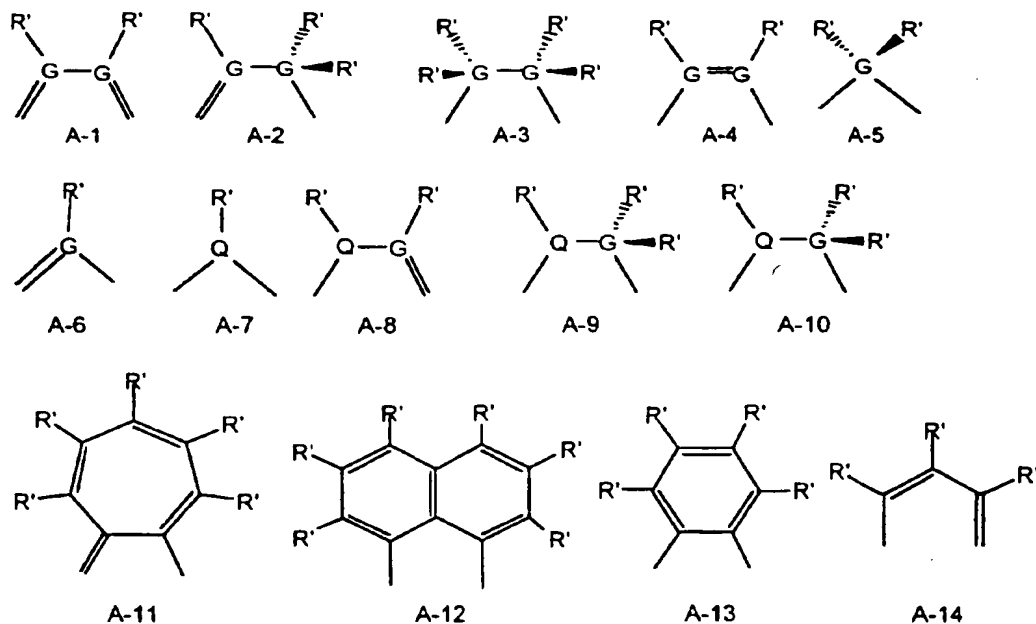
wherein M is a Group 9, 10, or 11 metal, preferably a first row metal, also preferably a d<sup>6</sup>, d<sup>8</sup> or d<sup>10</sup> metal, most preferably d<sup>8</sup>; L is a bidentate ligand that stabilizes a square planar geometry and charge balances the oxidation state of MX<sub>r</sub>; each X is, independently, a hydride radical, a hydrocarbyl radical, a substituted hydrocarbyl radical, a halocarbyl radical, a substituted halocarbyl radical, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals; or two X's are joined and bound to the metal atom to form a metallacycle ring containing from about 2 to about 20 carbon atoms; or one or more X can be a neutral hydrocarbyl containing donor ligand, e.g., an olefin, diolefin, or aryne ligand; and r = 0, 1, 2, or 3. When Lewis-acid activators, such as methylalumoxane, aluminum alkyls, or alkylaluminum halides, which are capable of donating an X ligand, as described above, to the transition metal component, are used, or when the ionic activator is capable of extracting X, one or more X may additionally be independently selected from the group consisting of a halogen, alkoxide, aryloxy, amide, phosphide or other univalent anionic ligand; two such X's joined to form an anionic chelating ligand; or, one or more neutral non-hydrocarbyl atom containing donor ligand, e.g., phosphine, amine, nitrile or CO ligand.

25 In a preferred embodiment of the invention, the bidentate ligand, L, is defined by the following formula:



wherein A is a bridging group containing a Group 13-15 element, each E is independently a Group 15 or 16 element covalently bonded to M; each R is independently a C<sub>1</sub>-C<sub>30</sub> containing radical or diradical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, m and n are independently 1 or 2 depending on the valency of E; and p is the charge on the bidentate ligand such that the oxidation state of MX<sub>r</sub> is satisfied.

In the most preferred embodiment of the invention, the bridging group, A, is defined by the following formulae:



wherein G is a Group 14 element especially C, Si, and Ge; Q is a Group 13 element especially B and Al; and R' are independently hydride radicals, C<sub>1</sub>-C<sub>30</sub> hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals, and

optionally two or more adjacent R' may form one or more C<sub>4</sub> to C<sub>40</sub> rings to give a saturated or unsaturated cyclic or polycyclic ring.

Also in the most preferred embodiment of the invention, each R is independently a  
5 bulky C<sub>1</sub>-C<sub>30</sub> containing radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, substituted organometalloid, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid. Bulky radical groups include phenyls, substituted phenyls, alkyls and substituted alkyls bonded to E through a tertiary carbon atom, alicyclic and polyalicyclic containing hydrocarbyls, particularly those bonded  
10 to E through a tertiary carbon and the like.

In the definitions above, the term "substituted" is as defined or refers to C<sub>1</sub>-C<sub>30</sub> containing radicals which are to be essentially hydrocarbyl, but may include one or more non-hydrocarbyl atoms (such as Si, Ge, O, S, N, P, halogen, etc.) in place of one or more  
15 carbon atoms.

In the very most preferred embodiment of this invention, M is a group 10 metal, E is a group 15 element especially nitrogen with m and n being one and p being zero, the bridge is as drawn in A-1, and R is a substituted phenyl group preferably substituted in at  
20 least the 2 and 6 positions with non-hydride R' groups. For high molecular weight polymers, R' is preferably C<sub>3</sub>-C<sub>30</sub>, preferably with a secondary or tertiary carbon atom bonded to the phenyl group. For lower molecular weight polymers, R in the 2 and 6 positions are preferably a C<sub>1</sub>-C<sub>2</sub> hydrocarbyl group or a C<sub>3</sub>-C<sub>10</sub> hydrocarbyl group with a primary carbon atom bonded to the phenyl group.

25 For the purposes of this patent specification, the terms "cocatalysts or activators" are used interchangeably and are defined to be any compound or component which can activate the late transition metal compound.

30 The late transition metal catalyst compounds according to the invention may be activated for polymerization catalysis in any manner sufficient to allow coordination

polymerization. This can be achieved, for example, when one X ligand can be abstracted and the other X will either allow insertion of the unsaturated monomers or will be similarly abstractable for replacement with an X that allows insertion of the unsaturated monomer. Traditional organometallic compound Ziegler cocatalysts may be utilized.

5 Additionally, the traditional activators of metallocene polymerization art are suitable activators; those typically include Lewis acids such as alumoxane compounds, and ionizing, anion precursor compounds that abstract one X so as to ionize the transition metal center into a cation and provide a counterbalancing, compatible, noncoordinating anion.

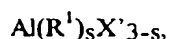
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In general, the late transition metal compound may be activated with an alumoxane, Ziegler cocatalyst, "noncoordinating anion" precursor compounds and halide salts of the Group 13-16 metals each of which is described more fully below.

15

The Ziegler cocatalyst will typically be an organometallic compound of a metal of Groups 1, 2, 12 or 13 of the Periodic table of elements. Preferred are organoaluminum compounds selected from the group consisting of aluminum alkyl, aluminum alkyl halide and aluminum halide. These can be represented by the formulae :

20



wherein  $\text{R}^1$  is independently a hydride or  $\text{C}_1$  to  $\text{C}_{10}$  hydrocarbyl radical including aliphatic, alicyclic or aromatic hydrocarbon radicals,  $\text{X}'$  is a halogen and  $s$  is an integer from 0 to 3; and,

25



which are hydrocarbylaluminum sesquihalides.

30 Examples include triethylaluminum, triisobutylaluminum, diethyl aluminumchloride,  $\text{Al}_2\text{Et}_3\text{Cl}_3$  and  $\text{Al}_2(\text{i-Bu})_3\text{Cl}_3$ .



When the activator is a Ziegler cocatalyst, the preferred molar ratio of late transition metal compound to Ziegler cocatalyst (typically measured as moles of aluminum) is from 1:1000 to 1:1, more preferably from 1:200 to 1:1 and most preferably from 1:100 to 1:1, although both higher and lower ratios may also be used.

5

Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators. The alumoxane component useful as catalyst activator typically is an oligomeric aluminum compound represented by the general formula  $(R^2-Al-O)_n$ , which is a cyclic compound, or  $R^2(R^2-Al-O)_nAlR^2_2$ , which is a linear compound. In the general alumoxane formula  $R^2$  is independently a  $C_1$  to  $C_{10}$  hydrocarbyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "n" is an integer from 1 to about 100. Most preferably,  $R^2$  is methyl and "n" is at least 4. Alumoxanes can be prepared by various procedures known in the art. For example, an aluminum alkyl may be treated with water dissolved in an inert organic solvent, or it may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an alumoxane. Generally, however prepared, the reaction of an aluminum alkyl with a limited amount of water yields a mixture of the linear and cyclic species of the alumoxane. Methylalumoxane and modified methylalumoxanes are preferred. For further descriptions see, U.S. Patent Nos. 4,665,208, 4,952,540, 5,041,584, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031 and EP 0 561 476 A1, EP 0 279 586 131, EP 0 516 476 A, EP 0 594 218 A1 and WO 94/10180, each being incorporated by reference for purposes of U.S. patent practice.

When the activator is an alumoxane, a preferred transition metal compound to activator molar ratio from 1:10000 to 1:1, more preferably from about 1:5000 to 1:1, even more preferably from about 1:1000 to 1:1, and most preferably from about 1:500 to 1:1. Higher or lower ratios may also be used.

In general, the late transition metal compound may be activated with an alumoxane, Ziegler cocatalyst, "noncoordinating anion" precursor compounds and halide salts of the Group 13-16 metals each of which is described more fully below.

30

The term "noncoordinating anion" as used for the ionizing, anion precursor compounds ("noncoordinating anion precursors") is recognized to mean an anion which either does not coordinate to said transition metal cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" noncoordinating anions are those which are not degraded to neutrality when the initially formed complex between the late-transition-metal catalyst compounds and the ionizing, anion precursor compounds decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral four coordinate metal compound and a neutral by-product from the anion. Noncoordinating anions useful in accordance with this invention are those which are compatible, stabilize the late-transition-metal cation in the sense of balancing its ionic charge, yet retain sufficient lability to permit displacement by an olefinically unsaturated monomer during polymerization. Additionally, the anions useful in this invention will be of sufficient molecular size to partially inhibit or help to prevent neutralization of the late-transition-metal cation by Lewis bases other than the polymerizable monomers that may be present in the polymerization process.

Descriptions of ionic catalysts, those comprising a transition metal cation and a non-coordinating anion, suitable for coordination polymerization appear in the early work in U.S. patents 5,064,802, 5,132,380, 5,198,401, 5,278,119, 5,321,106, 5,347,024, 5,408,017, WO 92/00333 and WO 93/14132. These teach a preferred method of preparation wherein metallocenes are protonated by an anion precursor such that an alkyl/hydride group is abstracted from a transition metal to make it both cationic and charge-balanced by the non-coordinating anion. These teachings are as to anion-providing precursors are suitable for the late transition metal catalysts of the present invention.

The use of ionizing ionic compounds not containing an active proton but capable of producing both the active metal cation and a noncoordinating anion is also known. See, EP-A-0 426 637, EP-A-0 573 403 and U.S. patent 5,387,568. Reactive cations other than the Brønsted acids include ferrocenium, silver, tropylium, triphenylcarbenium

and triethylsilylium, or alkali metal or alkaline earth metal cations such as sodium, magnesium or lithium cations. A further class of noncoordinating anion precursors suitable in accordance with this invention are hydrated salts comprising the alkali metal or alkaline earth metal cations and a non-coordinating anion as described above. The  
5 hydrated salts can be prepared by reaction of the metal cation-non-coordinating anion salt with water, for example, by hydrolysis of the commercially available or readily synthesized  $\text{LiB}(\text{pfp})_4$  which yields  $[\text{Li} \cdot x\text{H}_2\text{O}] [\text{B}(\text{pfp})_4]$ , where (pfp) is pentafluorophenyl or perfluorophenyl. Again, these activator compounds will be suitable for the catalyst systems of this invention.

10

Any metal or metalloid capable of forming a coordination complex, which preferably is resistant to degradation by water (or other Brönsted or Lewis Acids), may be used or contained in the anion. Suitable metals include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron,  
15 phosphorus, silicon and the like. The description of non-coordinating anions and precursors thereto of the documents of the foregoing paragraphs are incorporated by reference for purposes of U.S. patent practice.

An additional method of making the ionic catalysts uses noncoordinating anion  
20 precursors which are initially neutral Lewis acids but form the cation and anion upon ionizing reaction with the late transition metal compounds, for example tris(pentafluorophenyl) boron acts to abstract a hydrocarbyl, hydride or silyl ligand to yield a late-transition-metal cation and stabilizing non-coordinating anion; see EP-A-0 427 697 and EP-A-0 520 732 which are directed to metallocene catalyst systems. Ionic  
25 catalysts for coordination polymerization can also be prepared by oxidation of the metal centers of transition metal compounds by anionic precursors containing metallic oxidizing groups along with the anion groups, see EP-A-0 495 375. The description of non-coordinating anions and precursors thereto of these documents are similarly incorporated by reference for purposes of U.S. patent practice.

30

When the cation portion of an ionic non-coordinating precursor is a Brönsted acid such as protons or protonated Lewis bases, or a reducible Lewis acid such as ferricenium

or silver cations, or alkali metal or alkaline earth metal cations such as those of sodium, magnesium or lithium cations, the transition metal to activator molar ratio may be any ratio, but preferably from about 10:1 to 1:10; more preferably from about 5:1 to 1:5; even more preferably from about 2:1 to 1:2; and most preferably from about 1.2:1 to 1:1.2 with  
5 the ratio of about 1:1 being the most preferred. Similar ratios may be used for other noncoordinating anion precursor compounds.

The late transition metal catalyst compounds of this invention may also be activated with ionizing anion precursors including the halide salts of Group 13 -16 metals or  
10 metalloids, preferably the fluoride and oxyfluoride salts, e.g., those capable of providing the following anions:  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{TeOF}_6^-$  and  $\text{AsF}_6^-$ .

When halide salts of Group 13-16 metals or metalloids are used as the activator, the preferred total transition metal compound to activator molar ratio is preferably from  
15 10:1 to 1:10, more preferably from about 5:1 to 1:5, even more preferably from 2:1 to 1:2, and even more preferably from 1.2:1 to 1:1.2 with 1:1 being most preferred. Higher or lower ratios may also be used.

When using ionic catalysts of the late transition metal complexes comprising  
20 cations and non-coordinating anions, the total catalyst system can additionally comprise one or more scavenging compounds. The term "scavenging compounds" is meant to include those compounds effective for removing polar impurities from the reaction environment. Impurities can be inadvertently introduced with any of the polymerization reaction components, particularly with solvent, monomer and catalyst feed, and adversely  
25 affect catalyst activity and stability. Impurities can result in decreased, variable or even elimination of catalytic activity. The polar impurities, or catalyst poisons include water, oxygen, metal impurities, etc. While the late transition metal catalysts of the present invention can be less sensitive to impurities than metallocene catalyst systems, reduction or elimination of poisons remains a viable option. Preferably steps are taken before  
30 provision of such into the reaction vessel, for example by chemical treatment or careful separation techniques after or during the synthesis or preparation of the various

components; some minor amounts of scavenging compound can still normally be used in the polymerization process itself.

Typically the scavenging compound will be an organometallic compound such as the Group 13 organometallic compounds of U.S. patents 5,153,157, 5,241,025 and WO-A-91/09882, WO-A-94/03506, WO-A-93/14132, and that of WO 95/07941. Exemplary compounds include triethyl aluminum, triethyl borane, triisobutyl aluminum, methylalumoxane, isobutyl aluminoxane, and n-octyl aluminum. Those scavenging compounds having bulky or C<sub>8</sub>-C<sub>20</sub> linear hydrocarbyl substituents covalently bound to the metal or metalloid center being preferred to minimize adverse interaction with the active catalyst. When alumoxane or Ziegler cocatalyst is used as activator, any excess over the amount of late-transition-metal present will act as scavenger compounds and additional scavenging compounds may not be necessary. The amount of scavenging agent to be used with late transition metal cation-non-coordinating anion pairs is minimized during polymerization reactions to that amount effective to enhance activity.

The catalyst systems of this invention can additionally be prepared by combining in any order the bidentate ligand L, or a known precursor to it, with a suitable late transition metal complex, and an activator compound. For example, the bidentate ligand L precursor (2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=CH)<sub>2</sub> may be added to the late transition metal complex NiBr<sub>2</sub>-MeOCH<sub>2</sub>CH<sub>2</sub>OMe in a solvent such as toluene having the activator compound methylalumoxane dissolved therein. Optionally, oxidizing or reducing agents may be used additionally to achieve the preferred d<sup>6</sup>, d<sup>8</sup> or d<sup>10</sup> metal compounds. All reactants may be added in any order, or even essentially simultaneously.

A preferred process of polymerization is that conducted at high pressure, that is at from 200 to 3000 bar, preferably from 500 to 2500 bar, more preferably from 800 to 2500 bar, in a homogeneous single phase or two fluid phases, with or without unreactive diluents or solvents at temperatures generally above the melting point of the polymer being produced, e.g. 120°C - 225°C, preferably 120° - 170°C. Such processes are typically known and may include the use of scavenger compounds and catalyst deactivation or

killing steps, see for example U.S. patents 5,432,242 and 5,408,017, and International publications WO 92/14766 and WO 95/07941. Each of these documents and their U.S. counterparts are incorporated by reference for purposes of U.S. patent practice. Preferred catalyst deactivators, or killers, include high molecular weight, non-recyclable compounds, such as polyvinyl alcohol which exhibit the functional capacity to complex with the catalysts so as to deactivate them while not forming volatile polar by-products or residual unreacted compounds. In the high pressure, supercritical ethylene process, no solvent is used, however, small amounts of solvent may be introduced into the reactor as the catalyst carrier or diluent. Such a process is defined herein as being substantially in the absence of solvent.

Another preferred process in which any of the catalyst, cocatalyst and scavenger selections disclosed in this application can be advantageously practiced is that of a continuous, solution process operated at or above 90 °C to 120 °C, even to 150 °C or to 160 °C. Typically this process is conducted in an inert hydrocarbon solvent, linear, cyclic or branched aliphatic, or aromatic, at a pressure of from 20 to 200 bar (2000 to 20016 kPa), the disclosures of U.S. patent applications Ser. No. 08/426,363, filed April 21, 1995, and Ser. No. 08/545,973 filed October 20, 1995, provide relevant description. These documents also are incorporated by reference for purposes of U.S. patent practice.

The process in accordance with copending application, U.S. Ser. No. 08/244,948, filed 9 January, 1995, published as WO 93/11171, is also a preferred process. Its 2-phase suspension process is conducted at medium pressures of at least 50 bar and temperatures at least 10°C greater than the melting point of the polymer being prepared, e.g. 80°C to 250°C, preferably 90°C to 170°C. These documents are incorporated by reference for purposes of U.S. patent practice.

The catalysts of the invention, as illustrated by Brookhart, et al, supra, exhibit significant losses in  $M_n$  and  $T_m$ , and a related gain in the number of branches per 1000 carbon atoms when going from 0°C to 25°C. It is thus important in the processes above to utilize either ethylene concentrations or pressures, to compensate for the adverse effects observed. Thus, with increased concentration in ethylene in the high temperature solution

processes and in the high ethylene pressure processes illustrated above, the adverse effects are minimized and the benefits of the invention are optimized. Though losses in activity with increasing temperature are noted as well, the improvements represented by comparably increased  $M_n$ , comparably decreased branching (and consequent increase in  $T_m$ ), and efficiency permit the preparation of industrially useful polymers that are not permitted under the conditions in the prior art. Accordingly, the solution process can have ethylene pressures of 60 psia (414 kPa) to 365 psia (2517 kPa), preferably 80 psia (552 psia) to 365 psia (2517 kPa), more preferably 100 psia (689 kPa) to 350 psia (2413 kPa), even more preferably 120 psia (827 kPa) to 350 psia (2413 kPa), and most preferably 150 psia (1034 kPa) to 350 psia (2413 kPa). Preferred temperature ranges are at or above 90°C to 120 °C, even to 150 °C or to 160 °C.

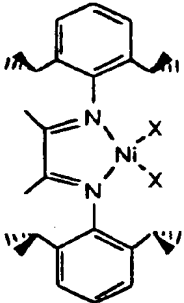
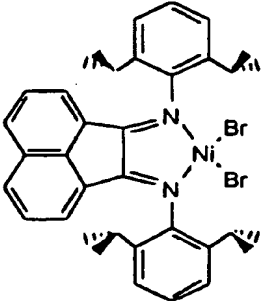
It is particularly suitable that the processes also should be designed or conducted such that the cocatalyst components, that is the transition metal compounds and the activator or cocatalyst compounds, are maintained separately until just prior to or during polymerization use in the chosen reactor. An example is the use of dual injection of each catalyst component directly into the reactor or the use of T- or multi-joint mixing chambers just prior to injection into the reactor. Alternatively the catalyst may be formed *in-situ* by the independent addition of activator, late transition metal catalyst precursor compound, and scavenger directly into the reactor.

In the processes discussed above, with the invention catalysts described in this application, unsaturated monomers, that is olefinically or ethylenically unsaturated monomers, may be polymerized so as to form polymer products having molecular weights (weight-average or  $M_w$ ) from about 500 to about  $3 \times 10^6$ . Most typically, the polymer products will have an  $M_w$  of from about 1000 to about  $1.0 \times 10^6$ . Suitable unsaturated monomers will include ethylene,  $C_3$ - $C_{20}$   $\alpha$ -olefins,  $C_4$ - $C_{20}$  cyclic olefins,  $C_4$ - $C_{20}$  non-conjugated diolefins,  $C_8$ - $C_{20}$  aromatic substituted olefins or  $C_{20}$ - $C_{1000}$   $\alpha$ -olefin macromers. Preferably the polymer products will be any of polyethylene homopolymers, ethylene copolymers, particularly polyethylene plastomers and elastomers. And, in view of the known tolerance of the catalysts to polar monomers, ethylenically unsaturated polar

monomers will additionally be polymerizable or copolymerizable. The preferred polar monomers include C<sub>4</sub>-C<sub>20</sub> olefins containing functional groupings such as esters, carboxylates, nitriles, amines, amides, alcohols, halides carboxylic acids and the like. More preferably vinyl esters, halides and nitriles. See also the monomers of U.S. Patent 5 4,987,200 which is incorporated by reference for the purpose of U.S. Patent Practice.

For the following examples, all molecular weights are weight average molecular weight unless otherwise noted. Molecular weights (weight average molecular weight (M<sub>w</sub>) and number average molecular weight (M<sub>n</sub>) were measured by Gel Permeation 10 Chromatography, unless otherwise noted, using a Waters 150 Gel Permeation Chromatograph equipped with a differential refractive index detector and calibrated using polystyrene standards. Samples were run in either THF (45°C) or in 1,2,4-trichlorobenzene (145 °C) depending upon the sample's solubility using three Shodex GPC AT-80 M/S columns in series. This general technique is discussed in "Liquid 15 Chromatography of Polymers and Related Materials III" J. Cazes Ed., Marcel Decker, 1981, page 207, which is incorporated by reference for purposes of U.S. patent practice herein. No corrections for column spreading were employed; however, data on generally accepted standards, e.g. National Bureau of Standards Polyethylene 1475, demonstrated a precision with 0.1 units for M<sub>w</sub>/M<sub>n</sub> which was calculated from elution times. The 20 numerical analyses were performed using Expert Ease software available from Waters Corporation.



Structure		
Designation	TM-2, X = Br	TM-4

#### Polymerization Method 1: High Pressure Polymerization

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The polymerizations of Table 1, below, were performed in a stirred 100 ml steel autoclave reaction vessel which was equipped to perform continuous Ziegler-Natta type polymerization reactions at pressures up to 2000 bar and temperatures up to 250 °C. The reaction system was equipped to measure temperature and pressure continuously and supplied continuously with purified compressed ethylene. Equipment for continuously introducing a measured flow of catalyst and cocatalyst solution, and equipment for collecting the polymer product were also part of the reaction system. Without the addition of a solvent, the polymerizations were performed with ethylene pressurized at 1350 bar to 1750 bar. No hydrogen was used. The catalyst solution is prepared by mixing continuous feeds of a solution of a specified concentration of the transition metal compound [acenaphthene bis-N,N'-(2,6-diisopropylphenyl) imine] dibromo nickel(II) (TM-4) in toluene with a methylalumoxane solution in toluene at the molar ratio of transition metal to total aluminum of 1 to 2000. This solution is continuously fed into the pressurized and heated reaction vessel. When the reaction conditions were stabilized polymer samples were collected from the continuously running polymerization reaction.

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Exact run conditions are collected in Table 1 including pressure (p) in bar, temperature (T) in °C, residence time (res. time) in seconds, catalyst concentration (cat. conc.) in mol-ppm as well as sampling time (sampl. time) in seconds, polymer yield (yield) in grams, ethylene conversion (conv.) in %, productivity (prod.) in kg polymer / mol catalyst and polymer characteristics including number of short chain branchings (SCB) per 1000 carbons determined by  $^{13}\text{C}$  - NMR: total, methyl- (Me), ethyl- (Et), propyl- (Pr), 1,3-diethyl ( $\text{Et}_2$ ), butyl- (Bu), amyl- , hexyl and larger branches (hex+); molecular weight data by GPC (diffuse refractive index): molecular weight ( $M_w$ ,  $M_z$ ) in dalton, molecular weight distribution (MWD).

An example of how to use the information contained in Table 1 follows describing example No. 1 using the reactor design as described above with a ratio of transition metal to aluminum of 1 to 2000. The transition metal compound and the methylalumoxane solution are fed into the stirred 100 ml autoclave pressurized to 1350 bar and heated to 120°C maintaining a catalyst concentration of 1.1597 mol-ppm with a catalyst residence time of 230 seconds. When temperature and pressure were stabilized a polymer sample was collected over a period of 791 s to yield 2.45 g of polymer product representing an ethylene conversion of 1.8% and a productivity of 415 kg polymer / mol transition metal catalyst.

$^{13}\text{C}$  - NMR analysis of the product gave a total number of SCB of 34.08 consisting of 23.2 methyl branches, 0.36 ethyl branches, 2.18 propyl branches, 3.08 1,3-diethyl branches, 0.91 butyl branches, 0.91 amyl branches and 3.44 hexyl or larger branches. GPC analysis (DRI) gave the following molecular weight data:  $M_w = 150\,900$  dalton,  $M_w/M_n = 2.073$  and  $M_z = 305\,200$  dalton.

TABLE 1

No.	p (bar)	T (C)	res. time (s)	cat. conc. (mol-ppm)	sampl. time (s)	yield (g)	conv. %	prod. (kg/mol)
1	1350	120	230	1.15968	791	2.45	1.8	415
2	1350	120	230	1.15968	1439	2.7	1.1	251
3	1750	120	185	0.81771	610	0.5	0.4	137
4	1750	120	186	0.82107	870	2.6	0.6	501
5	1350	165	185	0.79998	1001	1.3	0.8	232
6	1350	165	185	0.93331	858	0.6	0.4	107
7	1750	165	168	0.83953	904	1.7	1.1	296
8	1750	165	168	1.04961	422	1	1.4	298

TABLE 2

	total SCB/ 1000C	Me	Et <sup>1</sup>	Pr	1,3-Et <sub>2</sub> <sup>1</sup>	Bu	Amyl	Hex <sup>+</sup>	Mw	Mw/Mn	Mz
1	34.08	23.2	0.36	2.18	3.08	0.91	0.91	3.44	150900	2.07	305200
2	38.52	26.93	0.38	1.86	4.04	1.37	1.07	2.87	134200	2.64	252000
3	20.16	10.41	0.78	nm	1.56	0.91	2.6	3.9	175400	2.34	296700
4	17.09	11.99	0	0.36	1.6	1.24	0.7	1.2	167500	2.92	281900
5	41.13	25.09	0.37	2	4.94	2.32	1.65	4.76	92600	2.48	173300
6	46.9	29.48	0	2.22	5.92	3.08	1.87	4.33	91200	2.38	172200
7	28.79	19	0.41	1.24	3.38	1.73	0.56	2.47	98700	2.83	177800
8	30.19	20.3	0.16	1.12	3.09	1.46	1.06	3	108600	2.14	175700

<sup>1</sup> Total Et branches are determined by addition of the columns labelled Et and 1,3 - Et<sub>2</sub>

### Polymerization Method 2: Semi Batch Solution / Suspension Polymerizations in Hexane

Conditions of the polymerization examples are given in Table 3. Polymerizations were performed in a hot nitrogen purged 500 cc Zipperclave reactor (Autoclave Engineers) in dry hexane (about 250 to 300 cc) or toluene (400 cc) as the polymerization solvent / diluent. The catalyst solution was prepared in the dry box by mixing about 5 to 50 mg of late transition metal catalyst precursor TM-2 or TM-4 in 50 to 120 mg of toluene or 1,2-difluorobenzene for about 30 minutes. The cocatalyst used was methylalumoxane (MAO) in a 10 wt % toluene solution. Usually, 2.5 cc of the solutions was diluted to 10 cc with fresh toluene. The polymerizations were run by combining in-situ (in the reactor) the catalyst precursor and the cocatalyst solutions which had been previously added. The catalyst precursor solution was pumped to the reactor, and combined with the previously added cocatalyst solution, until the ethylene make-up flow became constant during the polymerization. The reactor temperature was controlled by steam/cooling water mixture flowing through the reactor jacket. The hexane or toluene was saturated with ethylene at the designated pressure and temperature prior to pumping the catalyst. By virtue of the limited solubility of the forming polymer in hexane, the polymer mass forms a solid phase suspended in hexane, thus making this process a slurry process. The catalyst in both instances is provided in solution, but is unsupported.

The polymerizations were run for about 30 minutes. At the end, the ethylene was vented and the reactor was cooled down. The reactor content was poured to a 1 L beaker and treated with isopropyl alcohol or acetone. The polymer solvent mixture was blown down with nitrogen or filtered to recover the polymer. The final product was dried under vacuum at 60 to 90°C for about 12 hours. The samples were analyzed by <sup>1</sup>H-NMR for branching and by GPC for molecular weight. Product characteristics are reported in Table 4.

### Polymerization Method 3: Semi Batch Solution/Suspension Polymerizations in Toluene.

Conditions of the polymerization examples are given in Table 3. Polymerizations were performed as in Method 2 with the following exceptions. A 1 L Zipperclave reactor (Autoclave Engineers) was used with toluene as polymerization solvent/diluent. The desired amount of late transition metal catalyst precursor was pumped into the reactor as a 1,2-difluorobenzene solution. The reactor contents were treated with acetone prior to recovery of the polymer. The polymer product was dried under vacuum at 50°C for about 12 hours. Product characterization are reported in Table 4.

TABLE 3

Ex	Cat.	Method	C <sub>2</sub> <sup>1</sup> psi	C <sub>2</sub> <sup>2</sup> kPa	° C	min	TM1 μmol	activ. μmol	activ. TM1 <sup>1</sup>	Yield g	g PE g cat. 2
C-1	TM-4	4	14.7	101	0	30	0.83	1532	1837	2.2	3667
C-2	TM-4	4	58.8	405	0	30	0.83	1532	1837	2.1	3500
C-3	TM-4	4	14.7	101	25	30	0.83	1532	1837	1.8	3000
9	TM-2	3	40	276	60	30	1.00	1532	1532	3	4839
10	TM-2	3	80	552	60	30	1.00	1532	1532	6.6	10645
11	TM-2	3	120	827	60	30	1.00	1532	1532	9.4	15161
12	TM-2	3	200	1379	60	30	1.00	1532	1532	11.5	18548
13	TM-2	3	280	1931	60	30	1.00	1532	1532	12.5	20161
14	TM-4	2	50	345	60	30	0.904	268.85	297	4.1	6270
15	TM-4	2	118	814	60	30	0.834	268.85	322	6.2	10350
16	TM-4	2	118	814	60	30	0.765	268.85	351	5.8	10600
17	TM-4	2	118	814	60	30	0.528	268.85	509	4.9	13000
18	TM-4	2	150	1034	60	30	0.375	268.85	717	2.9	11110
19	TM-4	2	240	1655	60	30	0.584	268.85	460	8.6	20480
20	TM-4	2	350	2413	60	30	0.320	268.85	840	6	26170

5 C-X = Polymerization Comparative X; TM = transition metal; PE = polyethylene;

C<sub>2</sub><sup>1</sup> = ethylene; activ. = activator.

<sup>1</sup>Unless noted the activator is MAO and activ./TM is the ratio of Al to TM based on the Al analysis of the MAO.

<sup>2</sup>Grams polyethylene per gram transition metal complex catalyst precursor.

Polymerization Method 4: Semi Batch Polymerization in Toulene.

This is the method of the comparative examples (C1-C3) disclosed in Brookhart, et  
5 al, supra.

**TABLE 4**  
**Batch Polymerization Process Examples.**

Ex	Cat.	Method	MW x10 <sup>-3</sup>	MWD	Me/1000 C <sup>1</sup>
C-1	TM-4	4	1600	2.4	24.0
C-2	TM-4	4	1400	2.3	5.0
C-3	TM-4	4	410	2.2	71.0
9	TM-2	3	397	3.3	92.7
10	TM-2	3	353	2.3	79.7
11	TM-2	3	543	2.5	71.4
12	TM-2	3	553	2.6	59.6
13	TM-2	3	557	2.7	55.1
14	TM-4	2	168	1.9	65.2
15	TM-4	2	267	2.1	65.2
16	TM-4	2	262	1.9	69.8
17	TM-4	2	235	2.0	73.2
18	TM-4	2	278	2.0	59.7
19	TM-4	2	338	2.0	48.0
20	TM-4	2	332	2.0	35.9

C-X = Polymerization Comparative X;

TM = transition metal;

<sup>1</sup>Me groups per 1000 carbons.

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**TABLE 5**  
**Predicted vs. Observed Branching**

Ex	Cat	°C	psia	kPa	Me/1000 C <sup>1</sup>	
C-1	TM-4	0	14.7	101	24	
C-2	TM-4	0	58.8	405	5	- .431 branch/psi vs. Ex. C-1
C-3	TM-4	25	14.7	101	71	+1.88 branch/°C vs. Ex. C-1
calc	TM-4	120	572	3944	0	Extrapolated from Ex. C-1
1	TM-4	120	19575	134975	34	
4	TM-4	120	25375	174968	17	

<sup>1</sup>Me groups per 1000 carbons.

From examination of Table 5, and examples C-1 and C-2 reported by Brookhart, et. al., supra, we observe that branching of the polymer C-1 decreased from 24 branches/1000 carbon atoms at 14.7 psia ethylene to 5 branches/1000 carbon atoms in C-2 at 58.8 psia ethylene. From this, one skilled in the art is led to believe that branching would decrease by 0.431 branches per one psia increase in pressure. Similarly, comparing examples C-1 and C-3 one skilled in the art is led to believe that branching would increase by 1.88 per °C of temperature increase.

From these observations, it would appear that extrapolating the data from Ex. C-1 to 120°C would result in an increase in branching to 250 branches per 1000 carbon atoms. Therefore, a concomitant increase in pressure to 594 psia (4095 KPa) would offset the temperature effects on branching and reduce the branches/1000 C to 0. As a consequence, one would expect that at 120°C, all pressures above 594 psia (4095 KPa) would result in 0 branches/1000 C. Surprisingly, however, at 120 °C and pressures as high as 19,575 psia (134,975 kPa) and 25,375 psia (174,968 kPa) significant branches/1000 C were still observed (34 branches/1000 C and 17 branches/1000 C, respectively) in the polymerization of Method 1 (Table 2).

The polymerization data of Brookhart, as shown in Tables 3 and 4, teaches that as pressure is increased, molecular weight decreases. Therefore, one skilled in the art would expect that under any set of otherwise comparative conditions, an increase in pressure would lead to a decrease in molecular weight of the polymer. However, examples 1-8 (of Tables 1 and 2) show that for catalyst TM-4 at both 120 °C and 165 °C, an increase in pressure from 19,575 psia (134,975 kPa) to 25,375 psia (174,968 kPa) leads to an increase in molecular weight of the polymer. Furthermore, as shown in Tables 3 and 4, data for both TM-2 and TM-4 at 60 °C and ethylene pressures from 40 psia (276 kPa) to 350 psia (2413 kPa) demonstrate the same trend of increasing molecular weight as ethylene pressure is increased, in contrast to the trend established by the polymerization data of Brookhart.

We claim:

CLAIMS:

1. A process for the polymerization of olefins comprising contacting ethylene and optionally, one or more ethylenically unsaturated monomers, with an unsupported  
5 late transition metal catalyst system comprising an activated Group 8, 9 or 10 transition metal compound stabilized by a bidentate ligand, at an ethylene pressure of at least 60 psia (413.7 kPa) and a reaction temperature equal to or greater than 90 °C.
- 10 2. The process of claim 1 wherein said contacting is in a solvent or diluent.
3. The process of claim 2 wherein said contacting is done in a continuous, solution process.
- 15 4. The process of claim 3 wherein the reaction temperature is 120 - 160 °C and the ethylene pressure is from 20 to 200 bar (2000 to 20016 kPa).
5. The process of claim 3 wherein the reaction temperature is 120 - 160 °C and the ethylene pressure is from 60 to 365 psia (414 to 2517 kPa).
- 20 6. The process of claim 1 wherein said transition metal system comprises a late transition metal compound activated by an alumoxane or Ziegler cocatalyst activator.
- 25 7. The process of claim 6 wherein the transition compound to activator ratio is from 1:1000 to 1:1.
8. The process of claim 1 wherein the transition metal system is derived from a late transition metal compound activated by a noncoordinating anion precursor  
30 compound.
9. The catalyst system of claim 8 wherein the noncoordinating anion precursor compound contains the noncoordinating anion tetrakis(perfluorophenyl)boron.
- 35 10. The catalyst system of claim 8 wherein the noncoordinating anion precursor compound is a halide salt of Group 13-16 metals or metalloids.



11. The catalyst of claim 8 wherein the metal complex is prepared by combining a transition metal compound with a noncoordinating anion precursor compound where the molar ratio of the transition metal compound to the ionizing anion precursor is from about 10:1 to 1:10.
- 5 12. The process of claim 8 wherein the transition metal system additionally comprises a scavenging compound.
- 10 13. A process for the polymerization of olefins comprising contacting ethylene and optionally, one or more ethylenically unsaturated monomer with an unsupported late transition metal catalyst system comprising an activated Group 8, 9 or 10 transition metal compound stabilized by a bidentate ligand, at an ethylene pressure of at least 200 bar ( $2.03 \times 10^4$  kPa) and a reaction temperature equal to or greater than 120 °C.
- 15 14. The process of claim 13 wherein said contacting is in a solvent or diluent.
15. The process of claim 14 wherein said contacting is done in a continuous, single phase process.
- 20 16. The process of claim 15 wherein the reaction temperature is 120 - 160 °C and the ethylene pressure is from 500 to 2500 bar ( $5.06 \times 10^4$  to  $2.53 \times 10^5$  kPa).
- 25 17. The process of claim 13 wherein said transition metal system comprises a transition metal compound activated by an alumoxane or Ziegler cocatalyst activator.
18. The process of claim 17 wherein the transition metal compound to activator ratio is from 1:1000 to 1:1.
- 30 19. The process of claim 13 wherein the transition metal system comprises a late transition metal compound activated by noncoordinating anion precursor compound.
- 35 20. The catalyst system of claim 19 wherein the noncoordinating anion precursor compound contains the noncoordinating anion tetrakis(perfluorophenyl)boron.

21. The catalyst system of claim 19 wherein the noncoordinating anion precursor comound is a halide salt of Group 13-16 metals or metalloids.
- 5 22. The catalyst of claim 19 wherein the metal complex is prepared by combining a transition metal compound with an ionizing anion precursor where the molar ratio of the transition metal compound to the ionizing anion precursor is from about 10:1 to 1:10.
- 10 23. The process of claim 19 wherein the transition metal system additionally comprises a scavenging compound.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 97/10419

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> C 08 F 4/80, C 08 F 10/02		
According to International Patent Classification (IPC) or to both national classification and IPC <sup>6</sup>		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) B 01 J, C 07 F, C 08 F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94/01471 A1 (EXXON CHEMICAL PATENTS INC.) 20 January 1994 (20.01.94), example 7, page 9, lines 27-30, page 14, lines 4-7, page 16, lines 21-26, page 18, lines 11-14, claims 1, 11, 12.	1-23
A	EP 0454231 A2 (THE UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL) 30 October 1991 (30.10.91), the whole document.	1-23
A	JOHNSON, L.K. et al. "New Pd(II)- and Ni(II)-Based Catalysts for Polymerization of Ethylene and Alpha-Ole-	1-23
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family		
Date of the actual completion of the international search 23 September 1997		Date of mailing of the international search report 10. 11. 97
Name and mailing address of the ISA European Patent Office, P.O. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016		Authorized officer PUSTERER e.h.

# INTERNATIONAL SEARCH REPORT

-2-

Intern. Application No  
PCT/US 97/10419

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	<p>fins. Journal of the American Chemical Society. 14 June 1995, Vol. 117, No. 23, pages 6414-6415, the whole document.</p> <p>--</p>	
A	<p>US 4716205 A (KLABUNDE) 29 December 1987 (29.12.87), claims 1,3, column 7, lines 47-53.</p> <p>--</p>	<p>1-7, 12-18</p>
A	<p>US 5324799 A (YANO et al.) 28 June 1994 (28.06.94), claims 1-5, examples 1-11.</p> <p>----</p>	<p>1-7, 12-18</p>

# ANHANG

zum internationalen Recherchen-  
bericht über die internationale  
Patentanmeldung Nr.

# ANNEX

to the International Search  
Report to the International Patent  
Application No.

# ANNEXE

au rapport de recherche inter-  
national relatif à la demande de brevet  
international n°

PCT/US 97/10419 SAE 163733

In diesem Anhang sind die Mitglieder  
der Patentfamilien der in obenge-  
nannten internationalen Recherchenbericht  
angeführten Patentdokumente angegeben.  
Diese Angaben dienen nur zur Unter-  
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family  
members relating to the patent documents  
cited in the above-mentioned inter-  
national search report. The Office is  
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relatifs aux documents de brevets cités  
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In Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
WO A1 9401471	20-01-94	EP A1 648230 JP T2 7509016 US A 5302124 US A 5304049	19-04-95 05-10-95 26-03-96 02-04-96
EP A2 454231	30-10-91	CA A2 2040808 EP A2 454231 JP A2 4327606 US A 5316739	21-10-91 15-01-92 17-08-92 14-05-96
US A 4716205	29-12-87	keine - none - rien	
US A 5324799	28-06-94	JP A2 3277610 CA A2 3037618 DE CO 6912055 DE T2 6912055 EP A2 446011 EP A3 446011 EP B1 446011	09-12-91 07-09-91 08-08-96 06-06-97 11-09-91 27-12-91 03-07-96